

# MEMBRANE SUPPORTED VOLTAMMETRY

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The development of microelectrodes has dramatically extended the timescale of electrode reactions accessible to study. Nano-scale electrified interfaces have been reported, but their widespread adoption has been hindered by the difficulties of reproducible production and characterization [1]. We have been developing arrays of micron and nano-scale electrodes using porous materials, such as commercially available alumina and polyester membranes. The electrified interface is located within the pores of the membrane, the pores act as a template controlling the dimensions of the interface.

There are two main aspects to the results to be presented:

(a) *Membrane Transport* We have used membrane materials to study transport to/from two types of electrochemical interface (i) the platinum/electrolyte solution interface and (ii) the interface between two immiscible electrolyte solutions (ITIES). For example, the transient response of interface of type (i) following a potential step, modified with a polyester membrane (pore diameter equals 30 nm), is compared against theory for coupled radial-linear diffusion at a recessed electrode [2] in Figure 1.

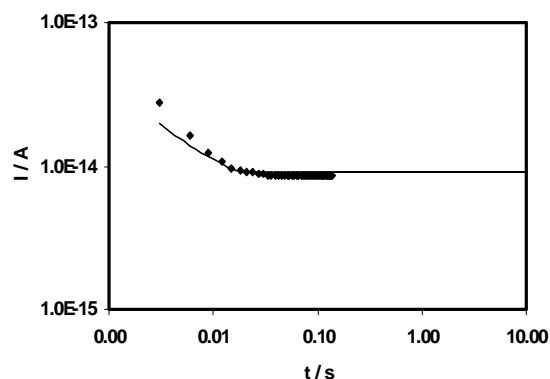


Figure 1. Chronoamperometry at a polyester membrane-modified interface of type (i).

The resultant modes of transport have been rationalized for known membranes structures. We note that methods such as the Scanning Electrochemical Microscope have been previously applied to the measurement of fluxes of ions [3] and redox -active molecules [4] through porous media. The voltammetric methods to be described here offer a novel method to characterize porous media (*i.e.* those where the pore structure is unknown). [5]

(b) *Interfacial Kinetics* The formation of micro (or nano-) electrode arrays leads to higher rates of mass-transport. These feature has been exploited to allow us to determine the rates of interfacial processes at interfaces of types (i) and (ii). In particular, over recent

years various groups have attempted to determine the rates of interfacial ion transfer at interfaces of type (ii). We have used membrane modification of the ITIES to generate arrays of micro-interfaces. Analysis of the resultant voltammograms has been carried out using a stationary ITIES configuration and an ITIES analogue of the rotating-membrane cell [6], where rotating-disc hydrodynamics were imposed on both the organic and aqueous phases. A typical experimental voltammogram, showing the characteristic steady-state current induced by the flow, is shown in Figure 2.

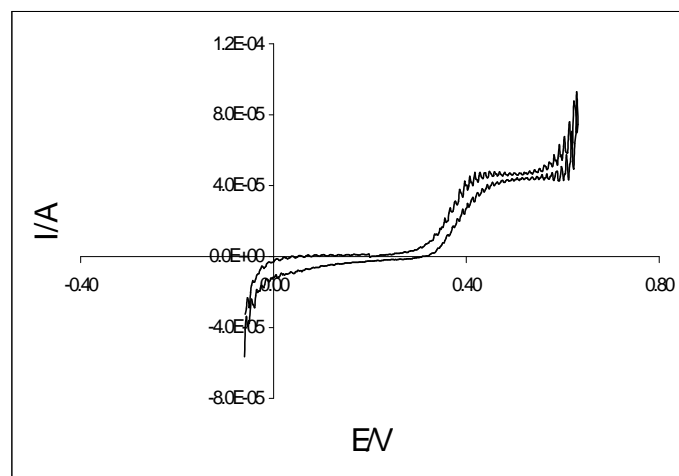


Figure 2: steady-state voltammogram obtained for the transfer of tetraethylammonium cation across a polyester membrane modified interface of type (ii).

Importantly, the rate constant characterizing the interfacial ion transfer process can be obtained from steady-state voltammetry, such as that shown above. We are also extending this work to ion transfer and electron transfer processes mediated by other types of porous media, including zeolite membranes [7].

## REFERENCES:

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